

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

Mo6998/LeA 33,907

U.S. APPLICATION NO. (If known, see 37 CFR 1.5

To be Assigned

10/069862

INTERNATIONAL APPLICATION NO.

PCT/EP00/08123

INTERNATIONAL FILING DATE

21 August 2000 (21.08.00)

PRIORITY DATE CLAIMED

01 September 1999 (1.09.99)

TITLE OF INVENTION

Thermoplastic Molding Materials Based on Particular Graft Rubber Constituents

APPLICANT(S) FOR DO/EO/US SUN, Liqing-Lee; EICHENAUER, Herbert and ALBERTS, Heinrich

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☒ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☒ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

Abstract page

PTO 1449 with listed references

U.S. APPLICATION NO. (known) 37 CFR 1.53 To be Assigned		INTERNATIONAL APPLICATION NO PCT/EP00/08123		ATTORNEY'S DOCKET NUMBER Mo6998/LeA 33,907	
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21. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1)-(5)):
 Neither international preliminary examination fee (37 CFR 1.482)
 nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
 and International Search Report not prepared by the EPO or JPO **\$1040.00**

International preliminary examination fee (37 CFR 1.482) not paid to
 USPTO but International Search Report prepared by the EPO or JPO **\$890.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
 but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$740.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
 but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
 and all claims satisfied provisions of PCT Article 33(1)-(4) **\$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30
 months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	16 - 20 =	0	x \$18.00	\$	
Independent claims	2 - 3 =	0	x \$84.00	\$	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$	
TOTAL OF ABOVE CALCULATIONS =				\$	890.00

☐ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above
 are reduced by 1/2. +

SUBTOTAL =

Processing fee of **\$130.00** for furnishing the English translation later than ☐ 20 ☐ 30
 months from the earliest claimed priority date (37 CFR 1.492(f)).

TOTAL NATIONAL FEE =

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
 accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

TOTAL FEES ENCLOSED =

	Amount to be refunded:	\$
	charged:	\$

CALCULATIONS PTO USE ONLY

a. ☐ A check in the amount of \$ _____ to cover the above fees is enclosed.


b. ☒ Please charge my Deposit Account No. 13-3848 in the amount of \$ 890.00 to cover the above fees.
 A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. 13-3848 A duplicate copy of this sheet is enclosed.

d. ☒ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
 information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:



00157
PATENT TRADEMARK OFFICE

SIGNATURE

Aron Preis
NAME

29,426
REGISTRATION NUMBER

10/069862

JC13 Rec'd PCT/PTO 26 FEB 2002

PATENT APPLICATION
Mo-6998
LeA 33,907

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION OF)
LIQING-LEE SUN ET AL) PCT/EP00/08123
SERIAL NUMBER: TO BE ASSIGNED)
FILED: HEREWITH)
TITLE: THERMOPLASTIC MOLDING)
MATERIALS BASED ON PARTICULAR)
GRAFT RUBBER CONSTITUENTS)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to the examination of the present patent application kindly amend the enclosed translation thereof as follows:

"Express Mail" mailing label number ET671453703US
Date of Deposit February 26, 2002

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on the date indicated above and is addressed to the Assistant Commissioner of Patents and Trademarks, Washington, D.C. 20231

Donna J. Veatch

(Name of person mailing paper or fee)

Signature of person mailing paper or fee

IN THE SPECIFICATION:

In page 1, please delete the title and insert the following in its stead:

--THERMOPLASTIC MOLDING MATERIALS BASED ON PARTICULAR
GRAFT RUBBER CONSTITUENTS--.

and add page 28, a page containing an abstract that reads as follows:

--THERMOPLASTIC MOLDING MATERIALS BASED ON PARTICULAR
GRAFT RUBBER CONSTITUENTS

ABSTRACT OF THE DISCLOSURE

A molding composition containing a graft polymer is disclosed. The graft is a product of a free-radical emulsion polymerization of resin-forming vinyl monomers in the presence of rubber present in latex form having a glass transition temperature of $\leq 0^{\circ}\text{C}$ using an initiator combination comprising a persulfate compound and a redox initiator system. The process for preparing the graft polymer entails adding the persulfate compound at the beginning of the graft polymerization reaction and a later addition of the redox initiator. The composition that features good gloss and flowability is suitable for the preparation of molded articles.--

IN THE CLAIMS:

Cancel Claims 14, 15 and 16.

Add the following:

- 17. The graft polymer prepared by the process of Claim 13.
18. A molded article comprising the graft polymer of Claim 17.
19. A molded article comprising the composition of Claim 1.--

REMARKS

The present amendment seeks to place the application in better conformance with U.S. practice. A page containing an Abstract of the Disclosure is enclosed. Entry of the amendment is requested.

Respectfully submitted,

By



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Attorney for Applicants
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s:/sr/ap0268

10065957 04450
205110 29859001

VERSION WITH MARKINGS TO SHOW CHANGES MADE:

IN THE SPECIFICATION:

In page 1, please delete the title and insert the following in its stead:

--THERMOPLASTIC MOLDING MATERIALS BASED ON PARTICULAR
GRAFT RUBBER CONSTITUENTS--.

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Thermoplastic moulding compositions based on certain graft rubber components

5 The present invention provides thermoplastic moulding compositions of the ABS type or of the ABS blend type containing improved graft rubber components which are obtained by emulsion polymerisation using specific initiator systems while defined reaction conditions are maintained.

10 Moulding compositions of the ABS type are two-phase plastics comprising

- 15 I) a thermoplastic copolymer in particular of styrene and acrylonitrile, in which the styrene may be replaced entirely or in part by α -methylstyrene or methyl methacrylate; this copolymer, also known as SAN resin or matrix resin, forms the outer phase;
- 20 II) at least one graft polymer which has been produced by a graft reaction of one or more of the monomers stated in I onto butadiene homo- or copolymer ("grafting backbone"). The graft polymer ("elastomer phase" or "graft rubber") forms the disperse phase in the matrix resin.

25 These blends of plastics may additionally contain further polymer components such as for example aromatic polycarbonate resins, polyester carbonate resins, polyester resins or polyamide resins, so resulting in so-called ABS blend systems.

30 Graft rubbers produced using redox initiator systems have proved particularly effective as impact modifiers for both ABS moulding compositions and ABS blend systems (*c.f.* for example EP 482 451 and the literature cited therein), wherein good toughness properties are generally achieved. Disadvantageously, surface gloss, elongation at break and thermoplastic flow properties are often inadequate or are subject to major variation.

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Donna J. Veatch

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Moreover, graft rubbers produced by redox initiation tend to have an elevated content of unreacted monomers which, while the content may indeed be reduced by adding metal ions (for example Fe ions) to the reaction mixture, impairs other properties (for example thermal stability, polymer colour).

5

There is accordingly a requirement for graft rubbers which do not exhibit these disadvantages and for a process by means of which ABS and ABS blend moulding compositions without the stated disadvantages may be produced.

10

It has now been found that moulding compositions having very good surface gloss, elevated elongation at break and good melt processability may be obtained without any negative effects on other properties if the graft rubber used is produced using specific combinations of initiator systems while maintaining defined reaction conditions.

15

The invention provides thermoplastic moulding compositions of the ABS type or of the ABS blend type containing

20

A) at least one elastic/thermoplastic graft polymer obtained by free-radical emulsion polymerisation of resin-forming vinyl monomers, preferably of compounds of the formulae (I) and (II) described below, particularly preferably of styrene and/or acrylonitrile, wherein styrene and/or acrylonitrile may be replaced entirely or in part by α -methylstyrene, methyl methacrylate or N-phenylmaleimide, in the presence of rubber present in latex form having a glass transition temperature of $\leq 0^\circ\text{C}$ using an initiator combination comprising a persulfate compound and a redox initiator system and

25

30

B) at least one copolymer of styrene and acrylonitrile, wherein styrene and/or acrylonitrile may be replaced entirely or in part by α -methylstyrene or methyl methacrylate or N-phenylmaleimide and optionally

C) at least one resin selected from the group of polycarbonates, polyesterarbonates, polyesters and polyamides,

characterised in that at the beginning of the graft polymerisation reaction the persulfate compound is added in quantities of 0.05 to 1.5 wt.%, preferably of 0.08 to 1.2 wt.% and particularly preferably of 0.1 to 1.0 wt.% (in each case relative to the monomers apportioned up to the time of addition of the redox initiator), after addition of 1 to 50 wt.%, preferably of 2.5 to 40 wt.%, particularly preferably of 5 to 30 wt.% and very particularly preferably of 7.5 to 25 wt.% of the monomers (in each case relative to the total quantity of monomers), the redox initiator components are added in quantities of 0.1 to 2.5 wt.%, preferably of 0.2 to 2 wt.% and particularly preferably of 0.5 to 1.5 wt.% (in each case relative to the monomers apportioned since the time of addition of the redox initiator).

Rubbers suitable for the production of the elastic/thermoplastic graft polymers according to the invention are in principle any rubbery polymers in emulsion form having a glass transition temperature of below 0°C.

The following may, for example, be used:

- diene rubbers, *i.e.* homopolymers of conjugated dienes having 4 to 8 C atoms such as butadiene, isoprene, chloroprene or the copolymers thereof with up to 60 wt.%, preferably up to 30 wt.% of a vinyl monomer, for example acrylonitrile, methacrylonitrile, styrene, α -methylstyrene, halostyrenes, C₁-C₄ alkylstyrenes, C₁-C₈ alkyl acrylates, C₁-C₈ alkyl methacrylates, alkylene glycol diacrylates, alkylene glycol dimethacrylates, divinylbenzene;
- acrylate rubbers, *i.e.* homo- or copolymers of C₁-C₁₀ alkyl acrylates, for example homopolymers of ethyl acrylate, butyl acrylate or copolymers with up to 40 wt.%, preferably no more than 10 wt.% of monovinyl monomers, for example styrene, acrylonitrile, vinyl butyl ether, acrylic acid (esters),

methacrylic acid (esters), vinylsulfonic acid. The acrylate rubber homo- or copolymers which are preferably used are those which contain 0.01 to 8 wt.% of divinyl or polyvinyl compounds and/or N-methylolmethacrylamide or N-methylolacrylamide or other compounds which act as crosslinking agents, for example divinylbenzene, triallyl cyanurate.

Polybutadiene rubbers, SBR rubbers with up to 30 wt.% of styrene incorporated by polymerisation and acrylate rubbers, in particular those having a core/shell structure, for example as described in DE-OS 3 006 804, are preferred.

Latices considered for the production of the graft polymers according to the invention are those having average particle diameters d_{50} of 0.05 to 2.0 μm , preferably of 0.08 to 1.0 μm and particularly preferably of 0.1 to 0.5 μm . The gel contents of the rubbers used may be varied within broad limits, preferably lying between 30 and 95 wt.% (determined using the wire cage method in toluene (*c.f.* Houben-Weyl, *Methoden der organischen Chemie, Makromolekulare Stoffe*, part 1, p. 307 (1961), Thieme Verlag Stuttgart)).

Mixtures of rubber latices having

- a) average particle diameters d_{50} of ≤ 320 nm, preferably of 260 to 310 nm, and gel contents of ≤ 70 wt.%, preferably of 40 to 65 wt.%, and
- b) average particle diameters d_{50} of ≥ 370 nm, preferably of 380 to 450 nm, and gel contents of ≥ 70 wt.%, preferably of 75 to 90 wt.%,

are very particularly preferred.

The rubber latex (a) here preferably has a width of the particle size distribution of 30 to 100 nm, particularly preferably of 40 to 80 nm, while that of the rubber latex (b)

is of 50 to 500 nm, particularly preferably of 100 to 400 nm (in each case measured as the d_{90} - d_{10} value of the overall particle size distribution).

5 The mixtures contain the rubber latices (a) and (b) preferably in a weight ratio of 90:10 to 10:90, particularly preferably of 60:40 to 30:70 (in each case relative to the particular solids content of the latices).

10 The average particle diameters are determined by ultracentrifugation (*c.f.* W. Scholtan, H. Lange, *Kolloid-Z. u Z. Polymere* 250, pp. 782-796 (1972)).

The stated gel content values relate to determination using the wire cage method in toluene (*c.f.* Houben-Weyl, *Methoden der organischen Chemie, Makromolekulare Stoffe*, part 1, p. 307 (1961), Thieme Verlag Stuttgart).

15 The rubber latices used may be produced by emulsion polymerisation, the necessary reaction conditions, auxiliaries and working methods being known in principle.

20 It is also possible initially to produce a finely divided rubber polymer using known methods and then to agglomerate it in known manner to establish the required particle size. Relevant techniques have been described (*c.f.* EP-B 0 029 613; EP-B 0 007 810; DD-PS 144 415; DE-AS 12 33 131; DE-AS 12 58 076; DE-OS 21 01 650; US-A 1 379 391).

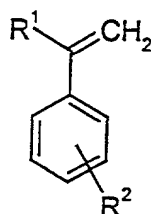
25 It is also possible to use the so-called seed polymerisation technique, in which a finely divided butadiene polymer, for example, is first produced and then further polymerised to yield larger particles by further reaction with monomers containing butadiene.

30 Emulsifiers which may be used are conventional anionic emulsifiers such as alkyl sulfates, alkyl sulfonates, aralkyl sulfonates, soaps of saturated or unsaturated fatty acids (for example oleic acid, stearic acid) as well as alkaline disproportionated or

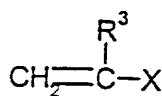
hydrogenated abietic or tall oil acid, with emulsifiers having a carboxyl group (for example salts of C₁₀-C₁₈ fatty acids, disproportionated abietic acid) preferably being used.

- 5 Rubber polymer latices may, in principle, also be produced by emulsifying complete rubber polymers in aqueous media (*c.f.* Japanese patent application 55 125 102).

Suitable graft monomers which are polymerised in the presence of the rubbery polymers present in emulsion form comprise virtually any compounds which may be
 10 polymerised in emulsion to yield thermoplastic resins, for example vinyl aromatics of the formula (I) or compounds of the formula (II) or mixtures thereof



(I)



(II)

in which

15

R¹ represents hydrogen or methyl,

R² represents hydrogen, halogen or alkyl having 1 to 4 carbon atoms in ortho,
 meta or para position,

20

R³ represents hydrogen or methyl

and

25 X represents CN, R⁴OOC or R⁵R⁶NOC,

in which

R⁴ means hydrogen or alkyl having 1 to 4 carbon atoms;

and

R⁵ and R⁶ mutually independently mean hydrogen, phenyl or alkyl having 1 to 4 carbon atoms.

Examples of compounds of the formula (I) are styrene, α -methylstyrene, p-methylstyrene and vinyltoluene. Compounds of the formula (II) are acrylonitrile and methyl methacrylate. Further monomers which are suitable in principle are, for example, vinyl acetate and N-phenylmaleimide.

Preferred monomers are mixtures of styrene and acrylonitrile, α -methylstyrene and acrylonitrile, of styrene, acrylonitrile and methyl methacrylate, as well as combinations of these monomer mixtures with N-phenylmaleimide.

Preferred graft polymers A) according to the invention are those which are obtained by graft polymerisation of styrene and acrylonitrile in a weight ratio of 90:10 to 50:50, preferably of 80:20 to 65:35 (wherein styrene may be replaced entirely or in part by α -methylstyrene or methyl methacrylate) in the presence of quantities of rubber, preferably polybutadiene, such that the resultant graft polymers have rubber contents of 20 to 80 wt.%, preferably of 30 to 75 wt.% and particularly preferably of 35 to 70 wt.%.

The graft polymers A) are here produced according to the invention in such a manner that, at the beginning of the graft reaction, at least one persulfate compound is added to the rubber latex or rubber latex mixture.

Suitable persulfate compounds are, for example and preferably sodium peroxydisulfate, potassium peroxydisulfate, ammonium peroxydisulfate, with potassium peroxydisulfate being a particularly preferred persulfate compound.

5 The persulfate compound is added in quantities of 0.05 to 1.5 wt.%, preferably of 0.08 to 1.2 wt.% and particularly preferably of 0.1 to 1.0 wt.% (in each case relative to the monomers apportioned before or from the start of addition of the persulfate compound).

10 Once the graft monomers have subsequently been further apportioned and once a quantity of 1 to 50 wt.%, preferably of 2.5 to 40 wt.%, particularly preferably of 5 to 30 wt.% and very particularly preferably of 7.5 to 25 wt.% has been added (in each case relative to the total quantity of monomers), a redox initiator system is added.

15 Suitable redox initiator systems generally consist of an organic oxidising agent and reducing agent, wherein heavy metal ions are preferably additionally present in the reaction medium.

20 Organic oxidising agents suitable according to the invention are for example and preferably di-tert.-butyl peroxide, cumene hydroperoxide, dicyclohexyl percarbonate, tert.-butyl hydroperoxide, p-menthane hydroperoxide or mixtures thereof, with cumene hydroperoxide and tert.-butyl hydroperoxide being particularly preferred. H_2O_2 may also be used.

25 Reducing agents usable according to the invention are preferably water-soluble compounds having a reducing action, preferably selected from the group comprising salts of sulfinic acid, salts of sulfurous acid, sodium dithionite, sodium sulfite, sodium hyposulfite, sodium hydrogen sulfite, ascorbic acid and the salts thereof, Rongalit C (sodium formaldehyde sulfoxylate), mono- and dihydroxyacetone, sugars
30 (for example glucose or dextrose), iron(II) salts, such as iron(II) sulfate, tin(II) salts, such as for example tin(II) chloride, titanium(III) salts, such as titanium(III) sulfate.

Particularly preferred reducing agents are dextrose, ascorbic acid (salts) or sodium formaldehyde sulfoxylate (Rongalit C).

- 5 The quantity of the redox initiator component is divided between the oxidising and reducing agents as follows:

10 The quantity of oxidising agent used generally amounts to 0.05 to 2.0 wt.%, preferably to 0.1 to 1.5 wt.% and particularly preferably to 0.2 to 1.2 wt.%. The quantity of reducing agent generally amounts to 0.05 to 1.5 wt.%, preferably to 0.08 to 1.2 wt.% and particularly preferably to 0.1 to 1.0 wt.%.

15 Conventionally, both the persulfate compound and the redox initiator components are used in the form of aqueous solutions, aqueous emulsions, aqueous suspensions or other aqueous dispersions.

The remaining monomers are then apportioned and polymerised to completion.

20 The invention furthermore provides a process for the production of graft rubbers by emulsion polymerisation using an initiator combination of a persulfate compound and a redox system, wherein

- i) the graft monomers are apportioned to the rubber latex,
- 25 ii) at the beginning of the graft polymerisation reaction the persulfate compound is added in quantities of 0.05 to 1.5 wt.% (relative to the monomers apportioned up to the time of addition of the persulfate compound) and
- 30 iii) after addition of 1 to 50 wt.% of the monomers (relative to the total quantity of monomers), the redox initiator components are added in quantities of 0.1

to 2.5 wt.% (relative to the monomers apportioned since the time of addition of the persulfate compound).

5 The reaction temperature during the production according to the invention of the graft rubbers A) may be varied within broad limits. The temperature is generally 25°C to 160°C, preferably 40°C to 90°C; very particularly preferably the temperature at the beginning of monomer apportionment differs from the temperature at the end of monomer apportionment by at most 20°C, preferably by at most 10°C and particularly preferably by at most 5°C.

10

Chain transfer agents may additionally be used during the graft polymerisation, preferably in quantities of 0.05 to 2 wt.%, particularly preferably in quantities of 0.1 to 1 wt.% (in each case relative to the total quantity of monomers).

15

Suitable chain transfer agents are, for example, n-dodecyl mercaptan, t-dodecyl mercaptan, dimeric α -methylstyrene, terpinolene and combinations of these compounds.

20

The above-stated compounds may be used as emulsifier during the graft polymerisation reaction.

25

The graft rubber latex A) is worked up using known methods, for example by spray drying or by addition of salts and/or acids, washing the precipitation products and drying the powder.

30

Vinyl resins B) which are used are preferably copolymers of styrene and acrylonitrile in a ratio by weight of 90:10 to 50:50, wherein styrene and/or acrylonitrile may be replaced entirely or in part by α -methylstyrene and/or methyl methacrylate; a proportion of up to 30 wt.% (relative to the vinyl resin) of a further monomer from the series maleic anhydride, maleimide, N-(cyclo)alkylmaleimide, N-(alkyl)phenylmaleimide may optionally also be used.

The weight average molecular weights (\overline{M}_w) of these resins may be varied within broad limits and are preferably between approx. 40000 and 200000, particularly preferably between 50000 and 150000.

5

Details relating to the production of these resins are described, for example, in DE-AS 2 420 358 and DE-AS 2 724 360. Resins produced by bulk or solution polymerisation and by suspension polymerisation have proved particularly suitable.

10 The proportion of the elastic/thermoplastic graft polymer (A) in the moulding compositions according to the invention may be varied within broad limits; the proportion is preferably from 1 to 80 wt.%, particularly preferably from 5 to 50 wt.%.

15 Necessary or convenient additives, for example antioxidants, UV stabilisers, peroxide scavengers, antistatic agents, lubricants, mould release agents, flame retardants, fillers or reinforcing materials (glass fibres, carbon fibres *etc.*) and colorants may be added to the moulding compositions according to the invention during production, working up, processing and final shaping.

20

Final shaping may be performed in conventional commercial processing units and comprises, for example, injection moulding, sheet extrusion optionally followed by thermoforming, cold forming, extrusion of tubes and profiles or calendering.

25 The ABS type moulding compositions according to the invention may be blended with other polymers (component C). Suitable blend partners are, for example, selected from at least one polymer selected from the group of polycarbonates, polyesters, polyestercarbonates and polyamides.

30 Suitable thermoplastic polycarbonates and polyestercarbonates are known (*c.f.* for example DE-AS 1 495 626, DE-OS 2 232 877, DE-OS 2 703 376, DE-OS

5



10

R⁷ and R⁸ mutually independently denote hydrogen, methyl or halogen, in particular hydrogen, methyl, chlorine or bromine,

20 m is an integer from 4 to 7, preferably 4 or 5,

n is 0 or 1,

R¹¹ and R¹² are individually selectable for each X and mutually independently mean
5 hydrogen or C₁-C₆ alkyl and

X' means carbon,

10 with carbonic acid halides, preferably phosgene, and/or with aromatic dicarboxylic acid dihalides, preferably benzenedicarboxylic acid dihalides, by phase interface polycondensation or with phosgene by polycondensation in the homogeneous phase (using the so-called pyridine process), wherein molecular weight may be adjusted in known manner by an appropriate quantity of known chain terminators.

15 Suitable diphenols of the formulae (III) and (IV) are, for example, hydroquinone, resorcinol, 4,4'-dihydroxydiphenyl, 2,2-bis-(4-hydroxyphenyl)propane, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 2,2-bis-(4-hydroxy-3,5-dimethylphenyl)propane, 2,2-bis-(4-hydroxy-3,5-dichlorophenyl)propane, 2,2-bis-(4-hydroxy-3,5-dibromophenyl)propane, 1,1-bis-(4-hydroxyphenyl)cyclohexane, 1,1-bis-(4-hydroxyphenyl)-
20 3,3,5-trimethylcyclohexane, 1,1-bis-(4-hydroxyphenyl)-3,3-dimethylcyclohexane, 1,1-bis-(4-hydroxyphenyl)-3,3,5-tetramethylcyclohexane or 1,1-bis-(4-hydroxyphenyl)-2,4,4-trimethylcyclopentane.

Preferred diphenols of the formula (III) are 2,2-bis-(4-hydroxyphenyl)propane and
25 1,1-bis-(4-hydroxyphenyl)cyclohexane and the preferred phenol of the formula (IV) is 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

Mixtures of diphenols may also be used.

30 Suitable chain terminators are, for example, phenol, p-tert.-butylphenol, long-chain alkylphenols such as 4-(1,3-tetramethylbutyl)phenol according to DE-OS 2 842 005,

monoalkylphenols, dialkylphenols having a total of 8 to 20 C atoms in the alkyl substituents according to DE-OS 3 506 472, such as p-nonylphenol, 2,5-di-tert.-butylphenol, p-tert.-octylphenol, p-dodecylphenol, 2-(3,5-dimethylheptyl)phenol and 4-(3,5-dimethylheptyl)phenol. The required quantity of chain terminators is in
5 general from 0.5 to 10 mol%, relative to the sum of diphenols (I) and (II).

Suitable polycarbonates or polyesterarbonates may be linear or branched; branched products are preferably obtained by incorporating from 0.05 to 2.0 mol%, relative to the sum of diphenols used, of trifunctional or greater than trifunctional compounds,
10 for example those having three or more than three phenolic OH groups.

Suitable polycarbonates or polyesterarbonates may contain aromatically attached halogen, preferably bromine and/or chlorine; they preferably contain no halogen.

15 They have average molecular weights (\overline{M}_w , weight average), determined for example by ultracentrifugation or light scattering, of 10000 to 200000, preferably of 20000 to 80000.

Suitable thermoplastic polyesters are preferably polyalkylene terephthalates, *i.e.* reaction products prepared from aromatic dicarboxylic acids or the reactive derivatives thereof (for example dimethyl esters or anhydrides) and aliphatic,
20 cycloaliphatic or arylaliphatic diols and mixtures of such reaction products.

Preferred polyalkylene terephthalates may be produced using known methods from
25 terephthalic acids (or the reactive derivatives thereof) and aliphatic or cycloaliphatic diols having 2 to 10 C atoms (*Kunststoff-Handbuch*, volume VIII, pp. 695 *et seq.*, Carl Hanser Verlag, Munich 1973).

In preferred polyalkylene terephthalates, 80 to 100, preferably 90 to 100 mol% of the
30 dicarboxylic acid residues are terephthalic acid residues and 80 to 100, preferably 90 to 100 mol% of the diol residues are ethylene glycol or 1,4-butanediol residues.

In addition to ethylene glycol or 1,4-butanediol residues, preferred polyalkylene terephthalates may contain 0 to 20 mol% of other aliphatic diols having 3 to 12 C atoms or cycloaliphatic diols having 6 to 12 C atoms, for example residues of

5 1,3-propanediol, 2-ethyl-1,3-propanediol, neopentyl glycol, 1,5-pentanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol, 3-methyl-1,3- and -1,6-pentanediol, 2-ethyl-1,3-hexanediol, 2,2-diethyl-1,3-propanediol, 2,5-hexanediol, 1,4-bis(β -hydroxyethoxy)benzene, 2,2-bis-(4-hydroxycyclohexyl)propane, 2,4-dihydroxy-1,1,3,3-tetramethylcyclobutane, 2,2-bis-(3- β -hydroxyethoxyphenyl)propane and 2,2-

10 bis-(4-hydroxypropoxyphenyl)propane (DE-OS 2 407 647, 2 407 776, 2 715 932).

The polyalkylene terephthalates may be branched by incorporation of relatively small quantities of tri- or tetrahydric alcohols or tri- or tetrabasic carboxylic acids, as are described in DE-OS 1 900 270 and US-A 3 692 744. Examples of preferred

15 branching agents are trimesic acid, trimellitic acid, trimethylolethane, trimethylolpropane and pentaerythritol. It is advisable to use no more than 1 mol% of the branching agent, relative to the acid component.

Particularly preferred polyalkylene terephthalates are those which have been produced solely from terephthalic acid and the reactive derivatives thereof (for example the dialkyl esters thereof) and ethylene glycol and/or 1,4-butanediol and mixtures of these polyalkylene terephthalates.

20

Preferred polyalkylene terephthalates also comprise copolyesters which are produced from at least two of the above-stated alcohol components: poly(ethylene glycol/1,4-butanediol) terephthalates are particularly preferred copolyesters.

25

Preferably suitable polyalkylene terephthalates generally have an intrinsic viscosity of 0.4 to 1.5 dl/g, preferably of 0.5 to 1.3 dl/g, in particular of 0.6 to 1.2 dl/g, in each case measured in phenol/o-dichlorobenzene (1:1 parts by weight) at 25°C.

30

Suitable polyamides are known homopolyamides, copolyamides and mixtures of these polyamides. These may comprise partially crystalline and/or amorphous polyamides.

- 5 Suitable partially crystalline polyamides are polyamide 6, polyamide 6,6, mixtures and corresponding copolymers of these components. Further partially crystalline polyamides which may be considered are those having an acid component entirely or partially consisting of terephthalic acid and/or isophthalic acid and/or suberic acid and/or sebacic acid and/or azelaic acid and/or adipic acid and/or cyclohexane-
10 dicarboxylic acid and a diamine component entirely or partially consisting of m- and/or p-xylylenediamine and/or hexamethylenediamine and/or 2,2,4-trimethylhexamethylenediamine and/or 2,2,4-trimethylhexamethylenediamine and/or isophoronediamine, and the composition of which is known in principle.
- 15 Further polyamides which may be mentioned are those produced entirely or in part from lactams having 7 to 12 ring C atoms, optionally together with one or more of the above-stated starting components.

20 Particularly preferred partially crystalline polyamides are polyamide 6 and polyamide 6,6 and mixtures thereof. Amorphous polyamides which may be used are known products. They are obtained by polycondensation of diamines, such as ethylene-diamine, hexamethylenediamine, decamethylenediamine, 2,2,4- and/or 2,4,4-trimethylhexamethylenediamine, m- and/or p-xylylenediamine, bis-(4-aminocyclohexyl)methane, bis-(4-aminocyclohexyl)propane, 3,3'-dimethyl-4,4'-
25 diaminodicyclohexylmethane, 3-aminomethyl-3,5,5-trimethylcyclohexylamine, 2,5- and/or 2,6-bis-(aminomethyl)norbornane and/or 1,4-diaminomethylcyclohexane with dicarboxylic acids such as oxalic acid, adipic acid, azelaic acid, decanedicarboxylic acid, heptadecanedicarboxylic acid, 2,2,4- and/or 2,4,4-trimethyladipic acid, isophthalic acid and terephthalic acid.

30

Copolymers which are obtained by polycondensing two or more monomers are also suitable, as are copolymers which are produced with the addition of aminocarboxylic acids such as ϵ -aminocaproic acid, ω -aminoundecanoic acid or ω -aminolauric acid or the lactams thereof.

5

Particularly suitable amorphous polyamides are the polyamides produced from isophthalic acid, hexamethylenediamine and further diamines such as 4,4'-diaminodicyclohexylmethane, isophoronediamine, 2,2,4- and/or 2,4,4-trimethylhexamethylenediamine, 2,5- and/or 2,6-bis-(aminomethyl)norbornene; or from isophthalic acid, 4,4'-diaminodicyclohexylmethane and ϵ -caprolactam; or from isophthalic acid, 3,3'-dimethyl-4,4'-diaminodicyclohexylmethane and lauro lactam; or from terephthalic acid and the isomer mixture of 2,2,4- and/or 2,4,4-trimethylhexamethylenediamine.

10

Instead of pure 4,4'-diaminodicyclohexylmethane, it is also possible to use mixtures of the positional isomers of diaminodicyclohexylmethane composed of

15

70 to 99 mol% of the 4,4'-diamino isomer

1 to 30 mol% of the 2,4'-diamino isomer

0 to 2 mol% of the 2,2'-diamino isomer and

20

optionally correspondingly more highly condensed diamines which are obtained by hydrogenating industrial grade diaminodiphenylmethane. Up to 30% of the isophthalic acid may be replaced by terephthalic acid.

The polyamides preferably have a relative viscosity (measured on a 1 wt.% solution in m-cresol at 25°C) of 2.0 to 5.0, particularly preferably of 2.5 to 4.0.

25

In the event that at least one polymer selected from the group of polycarbonates, polyesters, polyester carbonates and polyamides is additionally used, the quantity thereof amounts to up to 500 parts by weight, preferably up to 400 parts by weight

30

and particularly preferably up to 300 parts by weight (in each case relative to 100 parts by weight of A + B).

In the following Examples, unless otherwise stated, the stated parts are always parts
5 by weight and the stated percentages are always weight percentages.

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Examples

Example 1 (According to the invention)

5 58.5 parts by weight (calculated as solids) of a polybutadiene latex mixture (50%
having an average particle diameter d_{50} of 423 nm and a gel content of 82 wt.% and
10 50% having an average particle diameter d_{50} of 288 nm and a gel content of 56 wt.%,
both produced by free-radical polymerisation) are adjusted with water to a solids
content of approx. 20 wt.%, whereupon the temperature is raised to 75°C. 0.1 parts
by weight of potassium peroxydisulfate (dissolved in water) are then added and
6.225 parts by weight of a monomer mixture prepared from 73 wt.% of styrene and
27 wt.% of acrylonitrile are apportioned at a constant rate within 30 minutes at 75°C.
0.26 parts by weight of tert.-butyl hydroperoxide, 0.22 parts by weight of sodium
ascorbate and 35.275 parts by weight of a monomer mixture (styrene/acrylonitrile =
15 73:27) are then apportioned in parallel within 210 minutes, wherein the temperature
is maintained at 75°C. In parallel with the monomers, 1.72 parts by weight
(calculated as solid substance) of the sodium salt of a resin acid mixture (Dresinate
731, Abieta Chemie GmbH, Gersthofen, dissolved in alkalised water) are
apportioned over 4 hours.

20 After 1 hour's post-reaction at 85°C, the latex is cooled to 23°C; residual monomers
are then determined by gas chromatography using the headspace method (c.f. for
example B. Kolb in *Gaschromatographie in Bildern*, Wiley-VCH, Weinheim, 1999
and literature cited therein):

25

styrene:	3980 ppm
acrylonitrile:	460 ppm.

30 The graft latex is then coagulated by adding approx. 1 part by weight of a phenolic
antioxidant with a magnesium sulfate/acetic acid mixture and, after washing with
water, the resultant powder is dried at 70°C.

Example 2 (Comparison)

Example 1 is repeated, wherein once the polybutadiene latex mixture has been heated to 75°C, 0.039 parts by weight of t-butyl hydroperoxide and 0.033 parts by weight of sodium ascorbate are added and then 41.5 parts by weight of a monomer mixture of 73 wt.% of styrene and 27 wt.% of acrylonitrile, 0.221 parts by weight of t.-butyl hydroperoxide and 0.187 parts by weight of sodium ascorbate are apportioned at a constant rate in parallel within 4 hours.

10

Apportionment of the emulsifier and further processing are performed in a similar manner to Example 1.

Residual monomers:

15

styrene: 5750 ppm

acrylonitrile: 620 ppm

Example 3 (According to the invention)

20

Example 1 is repeated, wherein before the potassium peroxydisulfate is added, 6.225 parts by weight of the 73:27 styrene/acrylonitrile monomer mixture are added to the polybutadiene latex mixture and the remainder of the monomer mixture (35.275 parts by weight) is apportioned within 4 hours.

25

Addition of the redox initiator, apportionment of the emulsifier and further processing are performed in a similar manner to Example 1.

Residual monomers:

30

styrene: 3290 ppm

acrylonitrile: 290 ppm

Example 4 (Comparison)

5 Example 3 is repeated, wherein no potassium persulfate is added to the mixture of the polybutadiene latex mixture and 6.225 parts by weight of monomer mixture and the redox initiator components described in Example 2 are added as described in Example 2.

10 Apportionment of emulsifier and further processing are performed in a similar manner to Example 1.

Residual monomers:

15 styrene: 6660 ppm

acrylonitrile: 970 ppm

Production and testing of moulding compositions

20 23.8 parts by weight of the graft polymers described in Examples 1 to 4 are mixed in an internal kneader with 32.7 parts by weight of a styrene/acrylonitrile = 72:28 copolymer resin ($\overline{M}_w \approx 85000$), 42.6 parts by weight of a linear aromatic polycarbonate prepared from 2,2-bis-(4-hydroxyphenyl)propane (bisphenol A) having a relative viscosity of 1.26 (measured in CH_2Cl_2 at 25°C in the form of a 0.5
25 wt.% solution), corresponding to an \overline{M}_w of approx. 25000, and 0.75 parts by weight of pentaerythritol tetrastearate and then processed at 260°C to yield test specimens.

Notched impact strength is determined using the ISO 1801 A method on bars of dimensions 80 x 10 x 4 mm at room temperature and at -40°C.

Elongation at break, DR, is determined on F3 dumbbell test specimens during the determination of the tensile modulus of elasticity using the ISO 527 method.

Melt flow, MVR, is determined using the DIN 53 753 method at 260°C (5 kg load).

5

Surface gloss is evaluated visually as follows:

+ uniform, glossy surface

10 o reduced surface gloss

- non-uniform surface with glossy and matt areas.

15 As is clear from Table 1, the moulding compositions according to the invention exhibit improved flow properties and better gloss properties.

Table 1

Compositions and properties of polycarbonate/ABS moulding compositions

20

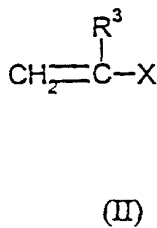
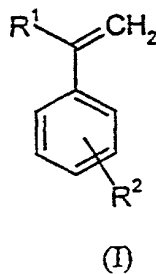
Example	Graft polymer used from Example	RT a_k (kJ/m ²)	-40°C a_k (kJ/m ²)	DR (%)	MVR (cm ³ /10 min)	Surface gloss
5	1	>70	>50	77	15.6	+
6 (Comp.)	2 (Comp.)	>70	>50	78	8.0	o
7	3	>70	>50	128	18.9	+
8 (Comp.)	4 (Comp.)	>70	>50	128	7.9	-

Patent Claims

1. Moulding composition containing
- 5 A) at least one elastic/thermoplastic graft polymer obtained by free-radical emulsion polymerisation of resin-forming vinyl monomers in the presence of rubber present in latex form having a glass transition temperature of $\leq 0^{\circ}\text{C}$ using an initiator combination comprising a persulfate compound and a redox initiator system and
- 10 B) at least one copolymer synthesised from styrene and acrylonitrile and optionally further comonomers and optionally
- 15 C) at least one resin selected from the group of polycarbonates, polyester carbonates, polyesters and polyamides,
- 20 characterised in that the graft polymer A) is produced in such a manner that, at the beginning of the graft polymerisation reaction the persulfate compound is added in quantities of 0.05 to 1.5 wt.% (relative to the monomers apportioned up to the time of addition of the redox initiator), after addition of 1 to 50 wt.% of the monomers (relative to the total quantity of monomers), the redox initiator components are added in quantities of 0.1 to 2.5 wt.% (relative to the monomers apportioned since the time of addition of the redox
- 25 initiator).
2. Moulding composition according to claim 1, characterised in that component A) is present in quantities of 1 to 80 wt.%.
- 30 3. Moulding composition according to claim 1, characterised in that the rubber used is a mixture of at least two rubber latices having

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- a) an average particle diameter d_{50} of ≤ 320 nm and a gel content of ≤ 70 wt.% and
- 5 b) an average particle diameter d_{50} of ≥ 370 nm and a gel content of ≥ 70 wt.%.
4. Moulding composition according to claim 1, characterised in that the elastic/thermoplastic graft polymer A) has a rubber content of 20 to 80 wt.%.
- 10 5. Moulding composition according to claim 1, characterised in that the resin-forming monomers in component A) are compounds of the formula (I) or (II) or mixtures thereof:



in which

R^1 represents hydrogen or methyl,

R^2 represents hydrogen, halogen or alkyl having 1 to 4 carbon atoms in ortho, meta or para position,

R^3 represents hydrogen or methyl

and

X represents CN , R^4OOC or $\text{R}^5\text{R}^6\text{NOC}$,

5 in which

R^4 means hydrogen or alkyl having 1 to 4 carbon atoms;

and

10

R^5 and R^6 mutually independently mean hydrogen, phenyl or alkyl having 1 to 4 carbon atoms.

6. Moulding composition according to claim 1, characterised in that the redox initiator system for the production of the graft polymer A) is selected from di-tert.-butyl peroxide, cumene hydroperoxide, dicyclohexyl percarbonate, tert.-butyl hydroperoxide, p-menthane hydroperoxide and H_2O_2 or mixtures thereof as the oxidising component and at least one water-soluble compound having a reducing action as the reducing component.

20

7. Moulding composition according to claim 6, wherein the oxidising agent is selected from cumene hydroperoxide, tert.-butyl hydroperoxide, p-menthane hydroperoxide or mixtures thereof.

25 8. Moulding composition according to claim 6, wherein the reducing agent is selected from salts of sulfinic acid, salts of sulfurous acid, sodium dithionite, sodium sulfite, sodium hyposulfite, sodium hydrogen sulfite, ascorbic acid and the salts thereof, Rongalit C (sodium formaldehyde sulfoxylate), mono- and dihydroxyacetone, sugars, iron(II) salts, tin(II) salts, titanium(III) salts.

30

9. Moulding composition according to claim 8, wherein the reducing agent is selected from dextrose, ascorbic acid or the salts thereof, sodium formaldehyde sulfoxylate or mixtures thereof.
- 5 10. Moulding composition according to claim 1, characterised in that potassium peroxydisulfate is used as the persulfate compound for the production of the graft polymer A).
- 10 11. Moulding composition according to claim 1, characterised in that the copolymer B) is synthesised from monomers selected from styrene, α -methylstyrene, acrylonitrile, methyl methacrylate, maleic anhydride, N-phenylmaleimide or mixtures thereof.
- 15 12. Moulding composition according to claim 1 additionally containing at least one resin selected from the group of polycarbonates, polyestercarbonates, polyesters and polyamides.
- 20 13. Process for the production of graft polymers containing rubber by emulsion polymerisation using an initiator combination of a persulfate compound and a redox initiator system, characterised in that
- 25 i) the graft monomers are apportioned to the rubber latex,
- ii) at the beginning of the graft polymerisation reaction the persulfate compound is added in quantities of 0.05 to 1.5 wt.% (relative to the monomers apportioned up to the time of addition of the persulfate compound)
- 30 iii) after addition of 1 to 50 wt.% of the monomers (relative to the total quantity of monomers), the redox initiator components are added in

quantities of 0.1 to 2.5 wt.% (relative to the monomers apportioned since the time of addition of the persulfate compound).

14. Process according to claim 10 for the production of graft polymers
5 containing rubber according to claim 1.
15. Use of the moulding compositions according to any of claims 1 to 14 for the production of mouldings.
- 10 16. Mouldings obtainable from moulding compositions according to any of claims 1 to 14.

1006986-0440-29869001

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum
Internationales Büro



(43) Internationales Veröffentlichungsdatum
8. März 2001 (08.03.2001)

PCT

(10) Internationale Veröffentlichungsnummer
WO 01/16230 A1

(51) Internationale Patentklassifikation⁷: C08L 55/02, C08F 4/40, 279/04

(21) Internationales Aktenzeichen: PCT/EP00/08123

(22) Internationales Anmeldedatum:
21. August 2000 (21.08.2000)

(25) Einreichungssprache: Deutsch

(26) Veröffentlichungssprache: Deutsch

(30) Angaben zur Priorität:
199 41 491.2 1. September 1999 (01.09.1999) DE

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(84) Bestimmungsstaaten (regional): ARIPO-Patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI-Patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Veröffentlicht:

- Mit internationalem Recherchenbericht.
- Vor Ablauf der für Änderungen der Ansprüche geltenden Frist; Veröffentlichung wird wiederholt, falls Änderungen eintreffen.

Zur Erklärung der Zweibuchstaben-Codes, und der anderen Abkürzungen wird auf die Erklärungen ("Guidance Notes on Codes and Abbreviations") am Anfang jeder regulären Ausgabe der PCT-Gazette verwiesen.

(54) Title: THERMOPLASTIC MOLDING MATERIALS BASED ON PARTICULAR GRAFT RUBBER CONSTITUENTS

(54) Bezeichnung: THERMOPLASTISCHE FORMMASSEN AUF BASIS BESTIMMTER PFROPFKAUTSCHUKKOMponenten

(57) Abstract: The invention relates to thermoplastic molding materials of the ABS type or of the ABS blend type. The inventive thermoplastic molding materials contain improved graft rubber constituents which can be obtained by carrying out emulsion polymerization while using special initiator systems and adhering to defined reaction conditions.

(57) Zusammenfassung: Gegenstand der Erfindung sind thermoplastische Formmassen vom ABS-Typ bzw. vom ABS-Blend-Typ, enthaltend verbesserte Pfropfkautschukkomponenten, die durch Emulsionspolymerisation unter Verwendung spezieller Initiatorsysteme und Einhaltung definierter Reaktionsbedingungen erhalten werden.

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#4

I, **FRAS** a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

THERMOPLASTIC MOLDING MATERIALS BASED ON PARTICULAR GRAFT RUBBER CONSTITUENTS

the specification of which is attached hereto,

or was filed on **August 21, 2000**

as a PCT Application Serial No. **PCT/EP00/08123**

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s), the priority(ies) of which is/are to be claimed:

199 41 491.2 (Number)	Germany (Country)	September 1, 1999 (Month/Day/Year Filed)
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I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose the material information as defined in Title 37, Code of Federal Regulations, §1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

(Application Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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FULL NAME OF SECOND INVENTOR <u>Herbert Eichenauer</u>		INVENTOR'S SIGNATURE <u>[Signature]</u>	DATE <u>30.01.02</u>
RESIDENCE <u>D 41539 Dormagen, Germany</u>		CITIZENSHIP <u>DEX</u>	<u>German</u>
POST OFFICE ADDRESS <u>c/o BAYER AKTIENGESELLSCHAFT, D 51368 Leverkusen, Germany</u>			
FULL NAME OF THIRD INVENTOR <u>Heinrich Alberts</u>		INVENTOR'S SIGNATURE <u>[Signature]</u>	DATE <u>1.02.02</u>
RESIDENCE <u>D 51519 Odenthal, Germany</u>		CITIZENSHIP <u>DEX</u>	<u>German</u>
POST OFFICE ADDRESS <u>Schulstr. 1a, D 51519 Odenthal, Germany</u>			
FULL NAME OF FOURTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF FIFTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SIXTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SEVENTH INVENTOR		INVENTOR'S SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			

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